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THEORY OF INTERNAL RELAXATION IN CHEMICAL KINETICS*

by

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ABSTRACT

For molecular systems with a relatively small number of degrees of freedom internal relaxation processes are described by a non-homogeneous master equation for non-diagonal elements of the density matrix. The theory is applied to internal vibrational relaxation and intramolecular rearrangement (isomerization) reactions. The general character and certain types of solutions of the master equation are investigated.

Author

1) Introduction

In the theory of chemical reactions the reaction process is often pictured as the consequence of two interfering mechanisms which may be named external and internal collisions. Sometimes one also refers to the latter mechanism as "redistribution of energy between different degrees of freedom". In many instances, so in the case of unimolecular reactions and of bimolecular reactions with long-living reaction complexes, it is the internal mechanism which plays the decisive role in transferring a molecule or supermolecule from one region of relative stability within the configuration space to another. The perturbation by the external collisions of a molecular system can then be assumed to remain localized within one of its chemical configurations, with other words, reaction in such cases is very unlikely to occur as the immediate consequence of an external collision.

Picturing the reaction by the internal mechanism was extremely fruitful in the theory of unimolecular reactions^{1,2,3)}

¹⁾ O. K. Rice, H. C. Ramsperger, J. Am. Chem. Soc. 49, 1617 (1927), 50, 617 (1928)

R. A. Marcus, O. K. Rice, J. Phys. Chem. 55, 894 (1951)

²⁾ L. S. Kassel, J. Phys. Chem. 32, 225 (1928)

³⁾ N. B. Slater, Theory of Unimolecular Reactions
Cornell, Ithaca, New York, 1959, p 22.

and we shall refer to it explicitly throughout this paper. One of the assumptions, used in specifying the internal

mechanism, is that the reactant molecules with internal energy E_i form a microcanonic ensemble with equilibrium properties (i.e., constant density in phase space over the reactant region of the energy shell $E_i \dots E_i + dE_i$, resp. commutativity of the density matrix with the Hamiltonian of the reactant-species). This implies the existence of an intramolecular relaxation process with a relaxation time short compared with the time between the external collisions. Since molecules have a very small number of degrees of freedom it is not at all evident whether and under which circumstances such internal relaxation mechanisms may be taken as granted. The reaction process itself also needs further clarification. Particularly in the case of an intramolecular rearrangement reaction (also termed "isomerization reaction") one again makes explicit use of the assumption that there is an intramolecular relaxation mechanism, since otherwise the molecule would remain oscillating between reactant and product configuration till the external collisions had damped these oscillations away. In the latter case, however, a first order rate process could never be observed.

From the viewpoint of statistical mechanics the problem of intramolecular rearrangement reactions is the more intriguing one since all energy levels of the reacting molecule are discrete and non-degenerate. The forthcoming treatment can easily be specialized to monomolecular decomposition reactions. It also contains the special case of internal vibrational relaxation.

To the knowledge of the author, the only treatment, of intramolecular rearrangements, different from the scheme used for monomolecular dissociation reactions was given by Golden and Peiser⁴⁾ who based their approach on the repeated random phases assumption. S. Golden⁵⁾ also focussed attention

4) S. Golden, A.M. Peiser, J. Phys. and Coll. Chem., 55, 789 (1951)

5) S. Golden, Suppl. Nuovo Cimento, 5, 540 (1957), 15, 335 (1960)
and private communication

on the problem of how to understand the intuitive concept of chemical species in terms of quantum mechanics which is of prime importance for the present case.

Intramolecular rearrangement reactions represent a problem by its own nature in statistical mechanics. The systems we are dealing with have a comparatively small number of degrees of freedom so that some of the assumptions, generally agreed on, for the derivation of a master equation do not hold. Furthermore, in contrast to the main goal of the statistical mechanical treatment of ordinary systems, except those with magnetic fields, where one calculates the time dependence of the diagonal elements of the density matrix, we are exclusively interested in the non-diagonal elements of $\rho(t)$. The master equation we are to derive will be non-homogeneous (reflecting the fact that the initial density matrix does not commute with the unperturbed Hamiltonian \mathcal{H}_0) and the solution at very large times will shape into a diagonal density matrix. The relaxation times for the non-diagonal matrix elements to disappear can then be related to internal vibrational relaxation and the rate of intramolecular chemical change. Rates of reactions calculated on the basis of a purely internal relaxation mechanism, will be meaningful as long as the relaxation time of the unperturbed system under the action of outer collisions is long compared with the time for relaxation by the internal perturbation.

2) Characterizing- Reactant- and Product Species in a System with Intramolecular Change

The concept of molecular species, as it is used in chemistry, has no correspondence in basic theories for the description of nature, like classical mechanics and quantum mechanics. The reason is that the chemical aspect of matter is an operational one which can be characterized by certain limited sets of measurements. Other properties of matter are considered to be beyond the scope of chemistry.

S. Golden⁵⁾ has given a comprehensive formal description of the operational structure of chemistry postulating the existence of complete sets of commuting observables which can be used to determine the chemical state of matter in accordance with the intuitive traditional concept of chemical species. For the purpose of the present investigation the construction of such a set of commuting observables will be instrumental. At the same time the limitations of the chemical viewpoint for molecular species which can convert into each other will become obvious.

In dealing with a certain class of chemical reactions, as a first step we have to characterize the properties of any set of measurements suitable for distinguishing between the different molecular species and for further determination of the chemical situation. Out of the wide range of chemically relevant measurements there may be selected different sets with commuting observables comprising only the minimal number of measurements necessary for complete determination of the chemical state of a system. Each such set can be divided into two parts so that it will contain measurements which serve the purpose to distinguish between different chemical species (e. g. molecules M_1 , M_2 , ... or clusters of

molecules M_1M_1 , M_1M_2 , ..., $M_1M_1M_1$, $M_1M_1M_2$, etc.) and also measurements which will complete the quantum mechanical information, so that an initial density matrix ρ_0 is uniquely determined.

Any two chemically relevant measurements must enable us to distinguish between at least two chemical species. Now from physical insight it is known that chemical species may always be characterized by the atoms (or ions) out of which they can be thought to be built up, furthermore by their "chemical structure" which usually refers to a certain range for the relative positions of the nuclei. "Chemical structure", however, may also be understood in a broader sense, comprising electrons localized with respect to some of the nuclei, thus allowing ions or even local excitations to appear as a chemical species. We may idealize any set of measurements for determining chemical structure by a single observable "configuration", denoted by K . For our purposes it is not necessary to introduce measurements of the elementary composition (numbers of electrons and atomic nuclei) explicitly.

In the case of an intramolecular rearrangement K will not even approximately commute with the Hamiltonian \mathcal{H} , nor will it commute with \mathcal{H}_0 , since energy and local coordinates do not commute. Nevertheless, there must be an observable related to the energy of a molecule in one of its chemical configurations. Let us assume there are only two chemical species involved, the configuration of which can be found by measuring K^I and K^{II} .

$$\text{tr}(\mathcal{K}^I \rho) = \frac{N_I}{N} \quad \text{and} \quad \text{tr}(\mathcal{K}^{\text{II}}, \rho) = \frac{N_{\text{II}}}{N} ,$$

where tr denotes the trace of a matrix, will then be the relative numbers of molecules in configurations I and II respectively and the initial density will commute with \mathcal{K}^I :

$$[\mathcal{K}^I, \rho_0] = 0$$

The Hamiltonian and also the unperturbed Hamiltonian must now be divisible into the following parts

$$\mathcal{H}_0 = \mathcal{H}_0^I + \mathcal{H}_0^{\text{II}} + \mathcal{H}_0^{I,\text{II}}$$

$$\mathcal{H} = \mathcal{H}^I + \mathcal{H}^{\text{II}} + \mathcal{H}^{I,\text{II}}$$

where

$$[\mathcal{H}_0^I, \mathcal{K}^I] = 0, \quad [\mathcal{H}^I, \mathcal{K}^I] = 0$$

and

$$[\mathcal{H}_0^{\text{II}}, \mathcal{K}^{\text{II}}] = 0, \quad [\mathcal{H}^{\text{II}}, \mathcal{K}^{\text{II}}] = 0$$

\mathcal{H}^I and \mathcal{H}^{II} are representing the non-reacting species I and II. The bound eigenfunctions of \mathcal{H}^I and \mathcal{H}^{II} , also of \mathcal{H}_0^I and $\mathcal{H}_0^{\text{II}}$, must then be localized in the regions of the respective chemical configurations. Thus, the eigenfunctions $|\alpha'_I\rangle, |\alpha'_\text{II}\rangle$ and $|\alpha_I\rangle, |\alpha_\text{II}\rangle$, satisfying

$$\mathcal{H}^I |\alpha'_I\rangle = E_{\alpha'}^I |\alpha'_I\rangle$$

and

$$\mathcal{H}^{\text{II}} |\alpha'_\text{II}\rangle = E_{\alpha'}^{\text{II}} |\alpha'_\text{II}\rangle$$

$$\mathcal{H}_0^I |\alpha_I\rangle = E_{\alpha}^I |\alpha_I\rangle$$

$$\mathcal{H}_0^{\text{II}} |\alpha_\text{II}\rangle = E_{\alpha}^{\text{II}} |\alpha_\text{II}\rangle$$

will be eigenfunctions of \mathcal{K}^I and \mathcal{K}^{II} , with

$$\mathcal{K}^I |\alpha'_I\rangle = |\alpha'_I\rangle$$

$$\mathcal{K}^I |\alpha'_\text{II}\rangle = 0$$

$$\mathcal{K}^I |\alpha_I\rangle = |\alpha_I\rangle$$

$$\mathcal{K}^I |\alpha_\text{II}\rangle = 0$$

and similar equations for II.

If $\{|\alpha'_I\rangle, |\alpha'_\text{II}\rangle$ and also $\{|\alpha_I\rangle, |\alpha_\text{II}\rangle\}$ span the whole Hilbert

space \mathcal{K}^I and \mathcal{K}^{II} are projection operators. Moreover, since $|\alpha_I\rangle$ and $|\alpha_{II}\rangle$ are so strongly localized in the region of configuration I or II respectively, one configuration operator will be the orthogonal complement of the other. Thus

$$\mathcal{K}^I = 1 - \mathcal{K}^{II}$$

and

$$\text{tr}(\mathcal{K}^I \rho) + \text{tr}(\mathcal{K}^{II} \rho) = 1$$

Explicit constructions of \mathcal{H}_0^I , \mathcal{H}_0^{II} , \mathcal{K}^I and \mathcal{K}^{II} will be given in chpt. 3.

At the initial time $t=0$ an ensemble of molecules shall exist as chemical species I, i.e it is represented by a density matrix ρ_0 which is diagonal in the eigenrepresentation of \mathcal{K}^I and \mathcal{H}_0^I ,

$$\rho_0 = \sum_{\alpha_I} |\alpha_I\rangle P_{\alpha}^I \langle \alpha_I|.$$

This initial density will now decay in two ways:

- 1) leakage through the barrier between configuration I and II by tunnel-effect

and

- 2) transitions caused by the perturbation V .

A characteristic time, denoted by τ_i and τ_r , can be related to both of these processes. The time τ_m , available for the measurement of \mathcal{K}^I and \mathcal{H}_0^I , is therefore limited by τ_i and τ_r . To be sure that our ensemble has not changed considerably during the measurement we have to make $\tau_m \ll \min(\tau_i, \tau_r)$

A limited time for the measurement of \mathcal{K}^I and \mathcal{H}_0^I implies an uncertainty in the energy of the order τ_m^{-1} . On the other hand, if ρ_0 decays very rapidly by tunnel-effect and transitions, τ_m may become so large that the measurement of \mathcal{H}_0^I would spread out the energy of the ensemble way

above the barrier between configurations I and II. We shall exclude this interesting case here since it is beyond the scope of chemical kinetics, assuming $\tau_m' \ll E_{at}$,

where E_{at} is an energy of the order of the height of the barrier between regions I and II.

For nearly all chemical systems one can replace \mathcal{H}_0^I by two dependent measurements, \mathcal{E}^I and \mathcal{D}_e^I , \mathcal{E}^I representing the electronic state of the system, its eigenvalues e labelling sets of electronic quantum numbers, whereas \mathcal{D}_e^I denotes the observable related to the vibronic energy attributed to the electronic state e. \mathcal{E}^I and \mathcal{D}_e^I commute for at least most systems of chemical interest. More frequently, however, we shall find that \mathcal{E} and \mathcal{D}_e , the corresponding operators for the whole system, do not commute. Then Born-Oppenheimer separation does not hold and the ensemble of reactant molecules will change its distribution over the electronic states in the course of the reaction. Commuting operators, related to \mathcal{E} and \mathcal{D}_e , can nearly always be constructed in the following way. Denoting all electronic coordinates by x , all nuclear coordinates by X and letting \mathcal{T}_K and \mathcal{T}_e represent the kinetic energy operators of nuclei and electrons respectively, the total Hamiltonian is (in the absence of magnetic forces)

$$\mathcal{H} = \mathcal{T}_K + \mathcal{T}_e + U(x, X)$$

Solving

$$\{\mathcal{T}_e + U(X, x)\} |e\rangle = E_e |e\rangle$$

we can define

$$\mathcal{E} = \sum_e |e\rangle e \langle e|$$

and

$$\mathcal{D}_e = \langle e | \mathcal{H} | e \rangle$$

The diagonal part of the operator \mathcal{D}_e , given by

$$D_e^{(\alpha)} = \sum_e |e\rangle \langle e| \mathcal{H} |e\rangle \langle e|$$

will then commute with \mathcal{E} . By this method we can always construct sets of commuting operators, like

$$\begin{aligned} &K^I, \mathcal{E}^I, D_1^{I(\alpha)}, D_2^{I(\alpha)}, \dots \\ &K^{II}, \mathcal{E}^{II}, D_1^{II(\alpha)}, D_2^{II(\alpha)}, \dots \end{aligned}$$

It is clear that in cases like the above mentioned the non-diagonal part of D_e would occur as part of the perturbation operator V on a later stage of the theoretical treatment.

3) Quantum Theory of Internal Motion of a Molecule

Description of the reaction process requires the construction of a special set of eigenfunctions for the internal motion of a molecule⁶⁾. To this behalf we shall make

⁶⁾ see L. Hofacker, Z. Naturforsch. 18 a, 607 (1963)

two restrictive assumptions:

- 1) The whole reaction takes place under a fixed set e of electronic quantum numbers. \hat{E} will therefore commute with K , D and $D_e^{(d)}$.
- 2) Only the action of conservative forces is taken into account. Hence, Coriolis forces will be neglected after introducing a coordinate system which moves and rotates with the molecule.

If there are N atomic nuclei with coordinates X_1, \dots, X_{3N} in a coordinate system, rigidly fixed to the molecule, the forces acting on them will have a potential

$$U_J \tau (X_1, \dots, X_{3N})$$

which contains the centrifugal forces and depends therefore on the rotational quantum numbers J and τ (related to total angular momentum and one of its components).

The inner motion of the molecule is now represented by wave packets moving on the potential energy surface. The potential has the shape of two double moulds and the process of inner-molecular conversion takes place by the passage of wavepackets from one mould to the other. Solutions for the motion of waves in all regions of the many-dimensional potential energy surface are, of course, extremely difficult to obtain. However, since the wave packets represent thermal energy, their statistical

weights become lower and lower as their energy rises. Examining the problem from this angle we may say that the rate of the reaction will be determined by those wave packets which pass the saddle between the two moulds near its lowest point having little kinetic energy at the same time. Those wave-packets will follow rather closely a line of minimum curvature, termed the "reaction path", which leads from the bottom of one mould across the saddle point to the other mould.

Our concern now has to be a twofold one. In the first place we want to calculate the flux of wave-packets along the reaction path. This implies to establish a complete system with the property to factorize the motion along the reaction path from motion in other directions. On the other hand, we shall try to exploit the fact that the deviation of the center of wave packets from the reaction path is small.

First we determine a family of coordinate surfaces

$$(5) \quad \begin{aligned} \eta_2 &= \eta_2(X_1, \dots, X_{3N}) \\ &\vdots \\ \eta_M &= \eta_M(X_1, \dots, X_{3N}) \end{aligned}$$

(there are M internal degrees of freedom)

which shall have the property to contain the reaction path so that

$$(6) \quad \eta_2 = \eta_3 = \dots = \eta_M = 0$$

is a set of equations which has the point-set of the reaction path as its only solution. The coordinate surfaces $\eta_i = \text{const.}$ will then intersect with the reaction path.

In the system of skewed internal coordinates the kinetic energy operator is

$$(7) \quad \mathcal{T} = \frac{1}{2} G^{1/2} \sum_{ij=1}^M \frac{\partial}{\partial \eta_i} G^{-1/2} G^{ij} \frac{\partial}{\partial \eta_j} = \sum_{ij=1}^M \mathcal{T}^{ij}$$

(8a) where

$$G^{ij} = \sum_{\ell=1}^{3N} \frac{1}{m_\ell} \frac{\partial \eta_i}{\partial X_\ell} \frac{\partial \eta_j}{\partial X_\ell}$$

(8b) and

$$G = \det G^{ij}$$

We shall, from now on, distinguish the coordinate η_1 by denoting it as ξ . It is our aim to find a complete system which separates ξ from the other coordinates. This can, in general, not be obtained, yet, it is possible to find a complete set for the internal nuclear motion of the molecule where the eigenfunctions have the form:

$$(9) \quad \Psi(\xi, \eta_2, \dots, \eta_M) = \Phi(\xi) \varphi(\xi, \eta_2, \dots, \eta_M)$$

with the property that

$\Phi(\xi)$ behaves wave-like in ξ

$\varphi(\xi, \eta_2, \dots, \eta_M)$ is a wave-type function in η_2, \dots, η_M but not in ξ ; the variation in ξ will be found to depend on certain curvatures of the potential energy surface.

If we determine

$$\xi = \eta_1(X_1, \dots, X_{3N})$$

such that

$$(10) \quad G^{12} = G^{13} = \dots = G^{1M} = 0$$

the kinetic energy operator now reads

$$(11) \quad \begin{aligned} \mathcal{T} &= \mathcal{T}'' + \sum_{ij=2}^M \mathcal{T}^{ij} \\ &= \mathcal{T}^\xi + \mathcal{T}^v \end{aligned}$$

The Hamiltonian is

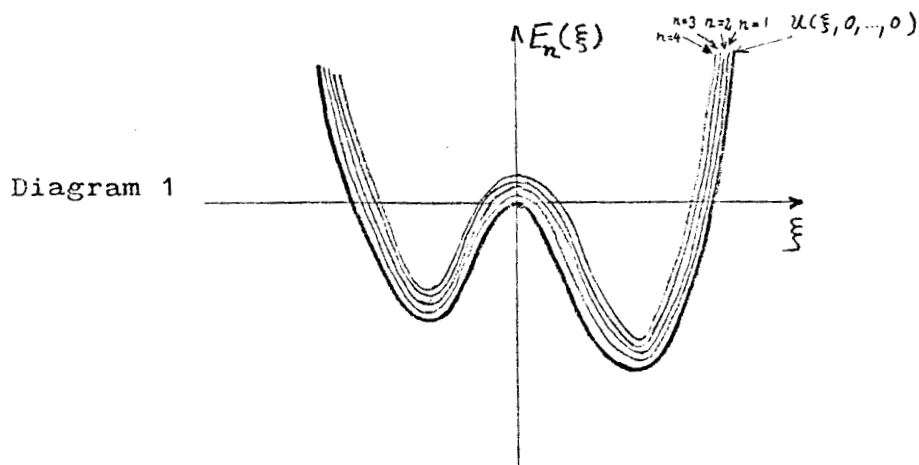
$$\begin{aligned}
 \mathcal{H} &= \mathcal{T} + \mathcal{U} \\
 (12) \quad &= \mathcal{T}^\xi + \mathcal{T}^v + \mathcal{U} \\
 &= \mathcal{T}^\xi + \mathcal{H}^v
 \end{aligned}$$

Note that \mathcal{T}^ξ depends on all internal coordinates but contains only differentiations with respect to ξ whereas \mathcal{H}^v depends on ξ only as a parameter.

Then the eigenvalue problem

$$(13) \quad \mathcal{H}^v |n\rangle = E_n(\xi) |n\rangle$$

produces $E_n(\xi)$ curves of the following kind



These curves do not intersect by similar reasons as spectroscopic terms. Furthermore, we may define the diagonal part of the operator \mathcal{T}^ξ with respect to $\{|n\rangle\}$:

$$(14) \quad \mathcal{T}_{(d)}^\xi = \sum_n |n\rangle \langle n| \mathcal{T}^\xi |n\rangle \langle n|$$

and solve the eigenvalue problem

$$(15) \quad \{\langle n| \mathcal{T}^\xi |n\rangle + E_n(\xi)\} |\tilde{n}\nu\rangle = E_{n\nu} |\tilde{n}\nu\rangle$$

where $|\tilde{n}\nu\rangle$ depends on ξ only. Then it is easy to see that

$$(16) \quad |n\nu\rangle = |n\rangle |\widetilde{n\nu}\rangle$$

is an eigenfunction for

$$(17) \quad \{\mathcal{T}_{(d)}^{\xi} + \mathcal{H}^{\nu}\} |n\nu\rangle = E_{n\nu} |n\nu\rangle$$

We write this equation in the form

$$(18) \quad \mathcal{H}_0 |n\nu\rangle = E_{n\nu} |n\nu\rangle$$

Since the non-diagonal part of \mathcal{T}^{ξ} , $\mathcal{T}_{(nd)}^{\xi}$ is defined by

$$(19) \quad \mathcal{T}^{\xi} = \mathcal{T}_{(d)}^{\xi} + \mathcal{T}_{(nd)}^{\xi}$$

the Hamiltonian is now split up into a main part and a perturbation \mathcal{V} :

$$(20) \quad \begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{T}_{(nd)}^{\xi} \\ &= \mathcal{H}_0 + \mathcal{V} \end{aligned}$$

Assuming that wave-packets which lead to reaction will not deviate much from the reaction path we may expand the potential in eq.(13) to second order terms in the η_k and use familiar methods for the treatment of small vibrations. In the vicinity of a point on the reaction path with coordinate ξ the coordinate surfaces $\eta_k = \text{const}$ may be substituted by their tangential planes,

$$(21a) \quad \eta_k = c_{k0}(\xi) + \sum_{c=1}^{3N} c_{kc}(\xi) X_c$$

or in matrix notation

$$(22b) \quad \eta = c_0 + C X.$$

After any initial choice of the coordinate surfaces η_k in this approximation all G^{ik} for $i, k \geq 2$ become functions of ξ only, hence

$$(23) \quad \mathcal{F}^v = \frac{1}{2} \sum_{i,k=2}^M G^{ik} \frac{\partial}{\partial \eta_i} \frac{\partial}{\partial \eta_k}$$

Expansion of the potential yields

$$(24) \quad \mathcal{U}(\xi, \eta_1, \dots, \eta_M) = \mathcal{U}(\xi, 0, \dots, 0) + \sum_{i=2}^M f_i(\xi) \eta_i + \sum_{i,k=2}^M \frac{1}{2} k_{ik}(\xi) \eta_i \eta_k$$

The $f_i(\xi)$ will in general not be zero wherefore we introduce new coordinates

$$(25) \quad \bar{\eta}_i = \eta_i - a_i(\xi) \quad \text{or} \quad \bar{\eta} = \eta - a$$

thus that

$$(26) \quad \bar{\mathcal{U}}(\xi, \bar{\eta}_1, \dots, \bar{\eta}_M) = \bar{\mathcal{U}}(\xi, 0, \dots, 0) + \sum_{i,k=2}^M \frac{1}{2} k_{ik}(\xi) \bar{\eta}_i \bar{\eta}_k$$

and

$$(27) \quad \mathcal{H}^v = \frac{1}{2} \sum_{i,k=2}^M G^{ik}(\xi) \frac{\partial}{\partial \eta_i} \frac{\partial}{\partial \eta_k} + \bar{\mathcal{U}}(\xi, 0, \dots, 0) + \sum_{i,k=2}^M \frac{1}{2} k_{ik}(\xi) \eta_i \eta_k$$

Now a new reaction path which may be called the "dynamic reaction path" can be defined by the set of equations (cf. eqs.(6))

$$(28) \quad \bar{\eta}_2 = \bar{\eta}_3 = \dots = \bar{\eta}_M = 0$$

Since all this holds for a fixed ξ we have to put

$$(29) \quad \bar{\xi} = \xi$$

In equ. (27) kinetic and potential energy can be made a sum of square terms by a transformation

$$(30) \quad \bar{\eta} = A \tilde{\eta} \quad , \quad \tilde{\eta} = \begin{pmatrix} \tilde{\eta}_2 \\ \vdots \\ \tilde{\eta}_M \end{pmatrix} .$$

so that it now reads

$$(31) \quad \mathcal{H}^v = \frac{1}{2} \sum_{i=2}^M \left\{ G_i(\xi) \frac{\partial^2}{\partial \tilde{\eta}_i^2} + h_i(\xi) \tilde{\eta}_i^2 \right\} + \bar{U}(\xi, 0, \dots, 0)$$

It can be shown that in the new coordinate system eqs.(10) still hold.

From (22b) and (25) follows

$$\begin{aligned} \bar{\eta} &= c_0 - a + Cx \\ &= \bar{c}_0 + Cx, \quad \bar{c}_0 = c_0 - a, \end{aligned}$$

and with (30) we have

$$\begin{aligned} A \tilde{\eta} &= c_0 + Cx \\ \tilde{\eta} &= A^{-1} c_0 + A^{-1} Cx \\ &= \tilde{c}_0 + \tilde{C}x; \\ (32) \quad \tilde{c}_0 &= A^{-1} \bar{c}_0 \\ \tilde{C} &= A^{-1} C \end{aligned}$$

Starting with (32) instead of (22) eqs.(10) become

$$\begin{aligned} G^{ik} &= \sum_{e=1}^{3N} \frac{1}{m_e} \frac{\partial \xi}{\partial x_e} \frac{\partial \eta_k}{\partial x_e} \\ &= \sum_{e=1}^{3N} \frac{1}{m_e} \frac{\partial \xi}{\partial x_e} \tilde{c}_{ke}(\bar{\xi}) \\ &= 0 \quad (k = 2, 3, \dots, M) \end{aligned}$$

or

$$(33) \quad \tilde{C} \tilde{d} = 0 \quad \text{where} \quad \tilde{d}_e = \frac{1}{m_e} \left(\frac{\partial \xi}{\partial x_e} \right), \quad \tilde{d} = \begin{pmatrix} \tilde{d}_1 \\ \vdots \\ \tilde{d}_{3N} \end{pmatrix}$$

On the other hand, the particular form of the Hamiltonian we are making use of was attained by choosing some \mathcal{A} which satisfies, according to (22), the equation

$$(34) \quad C\mathcal{A} = 0$$

Since \mathcal{A} is non-singular, (33) is fulfilled by putting

$$(35) \quad \tilde{\mathcal{A}} = \mathcal{A}$$

We can therefore, in the limit of small oscillations around the reaction path, change the η -coordinates to the $\tilde{\eta}$ without violating the condition (10).

After all, we can write the energy $E_n(\xi)$ in a more elaborate form

$$(36) \quad E_n(\xi) = \sum_{i=2}^M \omega_i(\xi) \left(n_i + \frac{1}{2} \right) + \bar{U}(\xi, 0, \dots, 0)$$

By this approach we have neglected all anharmonicities except those which occur along the reaction path. Undoubtedly, in chemical reactions the anharmonicities a wave-packet is subject to on its way straight towards the saddle will in general be more important than those of oscillatory motions which can not immediately lead to reaction.

We finally have to give a proper definition of the one-mould Hamiltonians \mathcal{H}_0^I and $\mathcal{H}_0^{\bar{I}}$ which one needed to construct the initial density matrix ρ_0 . From equ. (13) follows the set of curves $E_n(\xi)$. Let us denote the maximum in the middle of the n -th curve by ξ_n , then we may define

$$\mathcal{H}^v(\xi)|n\rangle = \mathcal{H}^{Iv}(\xi)|n_I\rangle = E_n^I(\xi)|n_I\rangle \quad \text{for } \xi < \xi_n$$

$$\mathcal{H}^v(\xi)|n\rangle = \mathcal{H}^{Iv}(\xi)|n_{II}\rangle = E_n^{II}(\xi)|n_{II}\rangle \quad \text{" } \xi > \xi_n$$

$|n_I\rangle$ and $|n_{II}\rangle$ will then be equal to $|n\rangle$ in their respective regions. Furthermore, choosing $E_n^I(\xi) = E_n^I(\xi_n)$ for $\xi \geq \xi_n$, we may define $|\widetilde{n}_{vI}\rangle$ and E_{nv}^I by

$$\{\langle n_I | \mathcal{H}^I | n_I \rangle - E_n^I(\xi)\} |\widetilde{n}_{vI}\rangle = E_{nv}^I |\widetilde{n}_{vI}\rangle$$

with a similar equation holding for mould II.

Thus \mathcal{H}_0^I and \mathcal{H}_0^{II} are given eigenfunctions and eigenvalues $|n_I\rangle|\widetilde{n}_{vI}\rangle$, E_{nv}^I and $|n_{II}\rangle|\widetilde{n}_{vII}\rangle$, E_{nv}^{II} respectively.

It shall be noted here that for the problem we are investigating only bound eigenfunctions, located in mould I or II, are of any interest.

\mathcal{K}^I and \mathcal{K}^{II} can then be defined by

$$\mathcal{K}^I = \sum_{nv_I} |nv_I\rangle \langle nv_I|, \quad \mathcal{K}^{II} = \sum_{nv_{II}} |nv_{II}\rangle \langle nv_{II}|.$$

4) Derivation of Relaxation Equation.

We shall now consider an isolated molecule with an initial density ρ_0 which is non-diagonal in the eigenstates of the total Hamiltonian \mathcal{H} . The crucial question is what the asymptotic behaviour in time of such a system might be. Molecules are finite systems and therefore it is not evident whether we shall be able to derive a master-equation describing the internal relaxation process. It can easily be recognized that not all the assumptions employed for infinite systems by van Hove and others^{7,8,9)} in order

7) L. van Hove, Physica 21, 517 (1955); 23, 441 (1957);
25, 268 (1959)

8) R.W. Zwanzig, Lectures in Theoretical Physics III, Boulder 1960, Interscience, New York, 1961, p. 106

9) A. Janner, Helv. Phys. Acta 35, 47 (1962); 36, 857 (1963)

to derive a master equation will hold. Nevertheless, we shall be able to establish an asymptotic solution of the von Neumann-equation which holds on a certain time scale. This can be done in a more straightforward way by direct investigation of the damping form of von Neumann's equation than by applying a Laplace-transform method^{10,11,12,13)}.

10) W. Kohn, J.M. Luttinger, Phys. Rev. 108, 590 (1957)

11) S. Nakajama, Progr. Theor. Phys. (Kyoto), 20, 948 (1958)

12) E.W. Montroll, Lectures in Theoretical Physics, III, Boulder 1960, Interscience, New York, 1961, p. 221

13) E.W. Montroll, Fundamental Problems in Statistical Mechanics Nijentode Castle 1961, North Holland, Amsterdam (subsequently cited as: Nijenrode 1961) p. 230

In applying the results to intramolecular rearrangements we shall make use of ideas, essential in all common theories of monomolecular reactions ³⁾, saying that under certain conditions the effect of collision with a heat-bath will be negligible.

Deriving the damping-form of von Neumann's equation we may follow the well-known procedure, yet keep in mind that ρ_0 will not commute with the Hamiltonian of the unperturbed system, \mathcal{H}_0 . Let the perturbation be the hermitian operator \mathcal{V} which may be identical with \mathcal{V}_{in} in chpt. 3. However, \mathcal{V} and \mathcal{H}_0 in principle may also comprise electronic terms. The Hamiltonian \mathcal{H} of the molecule will then be

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$$

and von Neumann's equation is

$$(37) \quad i\dot{\rho} = [\mathcal{H}, \rho]$$

Defining
$$\bar{\rho}(t) = e^{i\mathcal{H}_0 t} \rho(t) e^{-i\mathcal{H}_0 t}$$

we find by differentiation

$$\dot{\bar{\rho}}(t) = -i e^{-i\mathcal{H}_0 t} [\mathcal{V}, \rho] e^{i\mathcal{H}_0 t}$$

and by integration

$$\bar{\rho}(t) - \rho_0 = -i \int_0^t e^{-i\mathcal{H}_0 \tau} [\mathcal{V}, \rho(\tau)] e^{i\mathcal{H}_0 \tau} d\tau$$

or

$$\rho(t) = e^{-i\mathcal{H}_0 t} \rho_0 e^{i\mathcal{H}_0 t} - i \int_0^t e^{-i\mathcal{H}_0(t-\tau)} [\mathcal{V}, \rho(\tau)] e^{i\mathcal{H}_0(t-\tau)} d\tau$$

Substitution into equ. (37) gives

$$(38) \quad \begin{aligned} \dot{\rho} = & -i [\mathcal{H}_0, \rho] - i \left[\mathcal{V}, e^{-i\mathcal{H}_0 t} \rho_0 e^{i\mathcal{H}_0 t} \right] \\ & - \left[\mathcal{V}, \int_0^t e^{-i\mathcal{H}_0(t-\tau)} [\mathcal{V}, \rho(\tau)] e^{i\mathcal{H}_0(t-\tau)} d\tau \right] \end{aligned}$$

what may be termed the damping form of von Neumann's equation with an inhomogeneous term, the latter reflecting the non-commutativity of \mathcal{H}_0 and ρ_0 .

The eigenstates $|\alpha\rangle$ of the unperturbed Hamiltonian \mathcal{H}_0 , with

$$\mathcal{H}_0 |\alpha\rangle = E_\alpha |\alpha\rangle$$

may form an orthonormal basis of real wave functions since we shall be not interested in processes involving dissociation of the molecule. The eigenvalues E_α will be discrete and there are none but accidental degeneracies. Denoting

$$\omega_{\alpha\beta} = E_\alpha - E_\beta$$

and changing the integration variable we can write equ. (38) in matrix form as

$$\begin{aligned} \frac{d\rho_{\alpha\beta}}{dt} = & -i\omega_{\alpha\beta}\rho_{\alpha\beta} - i\sum_{\gamma}\{V_{\alpha\gamma}\rho_{\gamma\beta}e^{-i\omega_{\gamma\beta}t} - \rho_{\alpha\gamma}V_{\gamma\beta}e^{-i\omega_{\alpha\gamma}t}\} \\ & - \sum_{\gamma\epsilon}\{V_{\alpha\gamma}V_{\gamma\epsilon}\int_0^t e^{-i\omega_{\gamma\epsilon}\tau}\rho_{\epsilon\beta}(t-\tau)d\tau - V_{\alpha\gamma}V_{\epsilon\beta}\int_0^t e^{-i\omega_{\alpha\epsilon}\tau}\rho_{\gamma\epsilon}(t-\tau)d\tau \\ & - V_{\alpha\gamma}V_{\epsilon\beta}\int_0^t e^{-i\omega_{\gamma\beta}\tau}\rho_{\gamma\epsilon}(t-\tau)d\tau + V_{\gamma\epsilon}V_{\epsilon\beta}\int_0^t e^{-i\omega_{\alpha\epsilon}\tau}\rho_{\alpha\gamma}(t-\tau)d\tau \end{aligned} \quad (39)$$

Equation (39) is nothing but a different form of the von Neumann equation and therefore still reversible. However, we expect those terms depending on the square of the perturbation parameter to turn out as internal interactions ("internal collisions ") of the molecule which may in some sense give rise to an internal relaxation process. Even though equ. (39) itself is untreatable we shall try to construct an asymptotic solution which holds

for the order of magnitude of time which is of physical interest. To this behalf we first have to study the time-scales inherent in systems of molecular magnitude.

The asymptotic solution $\rho(t)$ we would like to establish shall hold for t of the order of the relaxation time. A necessary condition for such a $\rho(t)$ to exist is^{14,15,16)} that two characteristic times of the system ,

14) N.N. Bogoliubov, Studies in Statistical Mechanics, North-Holland, Amsterdam 1962, p.1.

15) L. Van Hove, La théorie des gaz neutres et ionisés, Les Houches 1958; Hermann, Paris 1960, p.151.

16) L. Van Hove, Nijenrode castle 1961, p.157.

an atomic time, τ_{at} , and a transversal time, τ_{tr} , are of entirely different orders of magnitude. If our physical interest in the system, characterized by the expectation values we want to calculate, requires a time of the order of magnitude τ_r and

$$(40) \quad \tau_{at} \ll \tau_r \ll \tau_{tr} ,$$

then certain simplifications can be made with equ. (39) which may allow us to establish the asymptotic form of $\rho(t)$. In fact, for chemical purposes we shall concentrate on a time-scale on which mayor changes in nuclear configuration will take place. Should the system be such that its asymptotic behaviour can in some sense be described as a relaxation process, then τ_r undoubtedly has to be of the order of the relaxation time.

It is very simple to identify τ_{at} and τ_{tr} for a molecular system. τ_{at} will be the average over the reciprocal distance between occupied levels,

$$\tau_a \approx \overline{\omega_{\alpha\beta}^{-1}} ,$$

Whereas τ_{tr} is the average distance between occupied adjacent levels α and α' ,

$$\tau_{tr} = \overline{\omega_{\alpha\alpha'}^{-1}}$$

Roughly, for molecules undergoing intramolecular conversion, we may put $\overline{\omega_{\alpha\beta}} = E_A$, E_A being the energy difference between the saddle point and the minimum point of the reactant mould on the potential energy surface.

Then, with $E_A \simeq 10^{-1} - 10^{-2}$ at u.,

$$\tau_{tr} \simeq E_A^{-1} \simeq 10 - 100 \text{ at.u.} \simeq 10^{16} - 10^{17} \text{ sec.}$$

Estimation of τ_{tr} requires the knowledge of the density of states in the saddle region. Using the harmonic approximation according to equ. (36) and extending it by assuming

$$\omega_i(\xi) = \omega_i(\xi_{0I}) = \bar{\omega}_i$$

where ξ_{0I} is the minimum of mould I, the condition for a potential curve to have its minimum below energy E_A is

$$(41) \quad \sum_{i=2}^M \bar{\omega}_i n_i \leq E_A - \frac{1}{2} \sum_i \bar{\omega}_i$$

The number of sets $\{n_2, \dots, n_M\}$, fulfilling equ. (41), is approximately (neglecting the zero-point energy in this equation):

$$Z(\bar{E}_A) = \int_{\sum_{k=2}^M \bar{\omega}_k n_k \leq \bar{E}_A} dn_1 dn_2 \dots dn_M = \frac{1}{\bar{\omega}_2 \bar{\omega}_3 \dots \bar{\omega}_M} \frac{1}{(M-1)!} \bar{E}_A^{M-1} \quad (3,17)$$

17) For a more precise estimate see
E.W. Schlag, R.A. Sandmark, J.Chem. Phys. 37, 168 (1962)

Let α be the average density of states in mould I of each of the curves $E_n(\xi)$. Then the density of states $\sigma(E)$ over the saddle region will be

$$\sigma(E_A) = 2(\bar{E}_A) \cdot \alpha$$

Assuming an average ratio

$$\frac{\bar{E}_A}{\omega_L} \approx 50$$

and a level density

$$\alpha = 10^3 (\text{at.u.})^{-1}$$

we have

$$\tau_{tr} \approx \sigma(E_A)^{-1}$$

and this time will be very large in comparison with τ_{at} and τ_r . For $M = 12, 24, 39$ we have $\tau_{tr} = 10^{15} \text{ at.u. } (10^{-2} \text{ sec})$, $10^{26} \text{ at.u. } (10^9 \text{ sec})$, $10^{39} \text{ at.u. } (10^{22} \text{ sec})$ respectively.

These numbers indicate, that condition (40) will be very well fulfilled by molecular systems of chemical significance. It is important to note that even for systems with a small number of degrees of freedom the level density is so high that the uncertainty relation will play a part throughout the process, as the eigenstates of the unperturbed Hamiltonian can never appear separated within times of the order of τ_r . The variation of the matrix elements $L_{\alpha\beta}$ of an observable L with α and β , where α is a state out of an energy intervall ΔE_a and β out of ΔE_b , will then be irrelevant if ΔE_a and ΔE_b are of the order τ_r^{-1} or smaller. Therefore we shall find it sufficient to establish an asymptotic solution $\rho(t)$ of (39)

which also varies slowly with E_α and E_β , the characteristic ranges of change being determined by ρ_0 and the matrix elements $V_{\alpha\beta}$. To this end we take several formal steps starting from equ. (39).

The sums in equ. (39) cannot readily be replaced by integrals since the matrix elements $V_{\alpha\beta}$ are not smooth functions of E_α and E_β . However, dividing the energy scale into equal intervals $\Delta E_1, \Delta E_2, \dots, \Delta E_a, \dots, \Delta E_b, \dots$ with numbers of states $g_1, g_2, \dots, g_a, \dots, g_b, \dots$ we may average $V_{\alpha\beta}$ over these intervals, writing

$$V_{\bar{\alpha}\beta} = \frac{1}{g_a} \sum_{\alpha \in a} V_{\alpha\beta},$$

where $\alpha \in a$ denotes that the states α are taken out of the interval ΔE_a . $V_{\bar{\alpha}\beta}$ will now be a smooth function of the parameter a , if

- A1) a large number of states lie in each interval ΔE_a .
- A2) the density of the states $g_a/\Delta E_a$ is a slowly varying function over the energy scale.

In addition, we shall require the length of the intervals ΔE , to be of an order of magnitude to fulfill a third condition

$$A3) \quad \Delta E \ll \tau_r^{-1}$$

According to A1) every interval will comprise many states of any kind. Following the procedure used in chpt. 3 to construct a basis for the molecule with a harmonic approximation one can see that to a given eigenfunction $|\alpha'\rangle$ we may find, within an energy distance of the order of the level splitting, another eigenfunction, $|\alpha''\rangle$, resembling $|\alpha'\rangle$ nearly perfectly,

except that one oscillator-function contained in $|\alpha\rangle$ has one node more whereas another one has one node less. Thus, given some $V_{\alpha\beta}$, we may select a large number of matrix elements with $\alpha \in a$ which differ only slightly from each other. Since conditions A2) and A3) are easily fulfilled by choosing ΔE_a suitably, the average $V_{\alpha\beta}$ may be considered a slowly varying function of E_a .

Now we may sum equ. (39) over all $\alpha \in a$ and $\beta \in b$. Using the notation

$$\sum_{\alpha \in a} \rho_{\alpha\beta} = \rho_{a\beta}$$

$$\frac{1}{g_a g_b} \sum_{\substack{\alpha \in a \\ \beta \in b}} \omega_{\alpha\beta} = \omega_{ab}$$

we may replace a \sum_r by $\sum_c g_c$ taken over suitable average values, ending up with

$$\begin{aligned} \frac{d\rho_{ab}}{dt} = & -i\omega_{ab} \rho_{ab} - i \sum_c \left\{ g_a V_{ac} \rho_{cb} e^{-i\omega_{cb}t} - g_b \rho_{ac} V_{cb} e^{-i\omega_{ac}t} \right\} \\ & - \sum_{c,e} \left\{ g_a g_c V_{ac} V_{ce} \int_0^t e^{-i\omega_{ce}\tau} \rho_{eb}(t-\tau) d\tau \right. \\ & \quad \left. - g_a g_b V_{ac} V_{eb} \int_0^t e^{-i\omega_{ab}\tau} \rho_{ce}(t-\tau) d\tau \right. \\ & \quad \left. - g_a g_b V_{ac} V_{eb} \int_0^t e^{-i\omega_{cb}\tau} \rho_{ce}(t-\tau) d\tau \right. \\ & \quad \left. + g_e g_b V_{ce} V_{eb} \int_0^t e^{-i\omega_{ae}\tau} \rho_{ac}(t-\tau) d\tau \right\}. \end{aligned} \quad (42)$$

Equ. (42), as it stands, may be treated further to find an asymptotic solution $\rho(t)$. More insight in the nature of the solution, however, can be gained by the procedure used in the following.

Since τ_r and τ_{tr} , for most molecular systems, are of such a different magnitude there may be an even coarser contraction over the energy scale for the asymptotic density matrix $\rho(t)$ which nevertheless will lead to the same expectation values. Having choosen a division of the energy scale into intervals ΔE which are as small as possible by order of magnitude, we may find a coarser division into intervals $\Delta E'$, suitable for simplifying the solution of equ.(42) in the following way. Let the intervals be

$$\Delta E'_1, \Delta E'_2, \dots, \Delta E'_A, \dots, \Delta E'_B, \dots$$

containing an even larger number of states

$$G_1, G_2, \dots, G_A, \dots, G_B, \dots$$

so that

$$G_A = \sum_{a \in A} g_a$$

and

$$B1) \quad G_A/g_a \quad \text{is a large number}$$

Furthermore, $\Delta E'$ shall be taken to be as large as possible by order of magnitude, yet fulfilling the requirements

- B 2) $\Delta E' \leq$ energy interval of characteristic change in $\rho_{\alpha\beta}$ with E_α and E_β (i.e. τ_m^{-1})
- B 3) $\Delta E' \leq$ energy interval of characteristic change of $V_{\alpha\bar{b}}$ with $E_{\bar{a}}$ or $E_{\bar{b}}$
- B 4) $\Delta E' \ll \tau_r^{-1}$

From the conditions B the requirement B3) will normally be the most restrictive one, thus determining $\Delta E'$. We shall be able to construct an asymptotic density matrix $\rho(t)$, where $\rho_{\alpha\beta}(t)$ will not vary appreciably with $\alpha \in \Delta E_A$ and $\beta \in \Delta E_B$. Our method is somewhat similar to the use of coarse-grained densities in classical statistical mechanics. 17,18,19)

17) P. Ehrenfest, Collected Scientific Papers, North Holland, Amsterdam, 1959, p. 213

18) D. Ter Haar, Rev. Mod. Phys. 27, 289 (1955)

19) N.G. Van Campen, Nijenrode Castle 1961, p. 173

If we sum equation (42) over $\sum_{a \in A} \sum_{b \in B}$ the first two terms on the right hand side can simply be written in terms of the indices A,B,C, whereas the collision terms can be given further treatment. Let us look in detail at the first collision integral; the others can be handled in analogous way:

$$\begin{aligned}
 (43) \quad & \sum_{a \in A} \sum_{c \in C} g_a g_c V_{a\bar{c}} V_{c\bar{e}} \int_0^t e^{-i\omega_{c\bar{e}}\tau} \rho_{eb}(t-\tau) d\tau = \\
 & = \sum_{c \in C} G_A g_c V_{A\bar{c}} V_{c\bar{e}} \frac{G_B}{\Delta E' g_B} \int_0^t \frac{e^{-i\omega_{cB+1}\tau} - e^{-i\omega_{cB}\tau}}{i\tau} \rho_{eb}(t-\tau) d\tau.
 \end{aligned}$$

Expanding $\rho(t-\tau)$ under the integral-sign in a Taylor-series

$$\rho(t-\tau) = \sum_{k=0}^{\infty} \frac{(-\tau)^k}{k!} \rho^{(k)}(t)$$

we have to evaluate the integrals

$$(44) \quad I_k = \int_0^t \frac{(-\tau)^k}{k!} \frac{e^{-i\omega_{cB+1}\tau} - e^{-i\omega_{cB}\tau}}{i\tau} d\tau.$$

The \mathcal{F}_k can be generated out of each other by differentiation.

$$\mathcal{F}_k = \frac{1}{i^k k!} \frac{\partial^k}{\partial \omega^k} \mathcal{F}_0$$

Since $\omega_{EB} \hat{\tau} \gg 1$ for nearly all terms under the sum in (43) it can be readily seen (introducing $\tau' = \omega_{EB} \hat{\tau}$ as a new variable of integration) that the upper limit in the integral (44) may be taken infinite. Then we have

$$\begin{aligned} \text{Re } \mathcal{F}_0 &= \Theta_B(E_z) \quad \text{where} \quad \Theta_B(E_z) = \begin{cases} 0 & \text{for } E_z > E_{B+1} \\ \pi & \text{for } E_B < E_z < E_{B+1} \end{cases} \\ \text{Im } \mathcal{F}_0 &= i \Delta E' \mathcal{P}\left(\frac{1}{\omega_{EB}}\right), \end{aligned}$$

\mathcal{P} denoting the Principal value,

or

$$(45) \quad \mathcal{F}_0 = \Theta_B(E_z) + i \Delta E' \mathcal{P}\left(\frac{1}{\omega_{EB}}\right)$$

Furthermore

$$\mathcal{F}_1 = 2\pi i (\delta_+(\omega_{EB+1}) - \delta_+(\omega_{EB}))$$

and

$$\begin{aligned} \mathcal{F}_k &= -\frac{2\pi}{i^k k!} \frac{\partial^{k-1}}{\partial \omega^{k-1}} (\delta_+(\omega_{EB+1}) - \delta_+(\omega_{EB})) \\ &= -\frac{2\pi}{i^k k!} (\delta_+^{(k-1)}(\omega_{EB+1}) - \delta_+^{(k-1)}(\omega_{EB})) \end{aligned}$$

$\delta_+(\omega)$ can also be represented by

$$(46) \quad \delta_+(\omega) = \lim_{\epsilon \rightarrow 0} \frac{1}{2\pi i} \frac{1}{\omega - i\epsilon}$$

and therefore

$$(47) \quad \delta_+^{(k-1)}(\omega) = \frac{(-1)^{k-1} (k-1)!}{2\pi i} \lim_{\epsilon \rightarrow 0} \frac{1}{(\omega - i\epsilon)^k}$$

The collision term (43) can now be written as follows:

$$(48) \quad \sum_{k=0}^{\infty} \sum_{c,e} \frac{G_A G_B}{\Delta E' g_B} g_c V_{Ac} V_{ce} \rho_{eb}^{(k)}(t) \mathcal{F}_k(\omega_{EB+1}, \omega_{EB})$$

$$= \sum_{k=0}^{\infty} \frac{G_A G_B}{\Delta E' g_B} \int_0^{\infty} dE_c dE_e g(E_c) V(E_A, E_c) V(E_c, E_e) \rho_{eb}^{(k)}(E_e, E_b; t) \mathcal{F}_k$$

$$= \sum_{k=0}^{\infty} \frac{G_A G_B}{\Delta E' g_B} \int_0^{\infty} dE_e \int_{-E_B}^{\infty} d\omega g(E_B + \omega) V(E_A, E_B + \omega) V(E_B + \omega, E_e) \rho_{eb}^{(k)}(E_e, E_b; t) \mathcal{F}_k^{(k)}$$

where $\omega = E_e - E_B$ was introduced as new integration variable.

We can now show that the ratio of two consecutive terms of the k-sum in (48) will be small.

The ω - integral in (48) has the general form

$$(49) \quad C_k = \int_{-E_B}^{\infty} d\omega F(\omega) \mathcal{F}_k(\omega + \Delta E', \omega)$$

Where $F(\omega)$ is slowly varying with ω . It is easy to see that the ratio between the terms with $k=1$ and $k=0$ is small.

We have

$$C_0 = \int_{-E_B}^{\infty} d\omega F(\omega) \mathcal{F}_0(\omega + \Delta E', \omega) = \int_{-E_B}^{\infty} d\omega F(\omega) \Delta E' 2\pi \delta_+(\omega)$$

$$C_1 = \int_{-E_B}^{\infty} d\omega F(\omega) \mathcal{F}_1(\omega + \Delta E', \omega) = \int_{-E_B}^{\infty} d\omega F(\omega) 2\pi i (\delta_+(\omega + \Delta E') - \delta_+(\omega))$$

$F(\omega)$ can be extended analytically outside the real axis. Since it is proportional to transition matrix elements V_{ab} we may also assume that $F(\omega)$ vanishes sufficiently strong at the infinite point. Furthermore, E_B is so large compared with $\Delta E'$ that the lower limit in (49) can be replaced by ∞ . Then, by (46) and

$$\int_{-E_B}^{\infty} \dots d\omega = \oint \dots d\omega,$$

the integration taken along $-\infty$ to $+\infty$ and encircling the positive imaginary halfplane, we have

$$\frac{\rho^{(1)}(t) C_1}{\rho^{(1)}(t) C_0} \simeq \frac{\frac{\rho}{\tau_r} (F(-\Delta E') - F(0))}{\rho \cdot \Delta E' \cdot F(0)} \simeq \frac{1}{\tau_r} \frac{F'(0)}{F(0)} \simeq \frac{F(0)/E_A}{\tau_r F(0)} = \frac{\tau_a}{\tau_r} \ll 1$$

Similarly, we find by (47)

$$\begin{aligned} \frac{\rho^{(k)}(t) C_k}{\rho^{(k-1)}(t) C_{k-1}} &\simeq \frac{\frac{\rho^{(k-1)}}{\tau_r} \cdot (F^{(k-1)}(-\Delta E') - F^{(k-1)}(0))}{\rho^{(k-1)} (F^{(k-2)}(-\Delta E') - F^{(k-2)}(0))} \simeq \frac{1}{\tau_r} \frac{F^{(k)}(0)}{F^{(k-1)}(0)} \\ &\simeq \frac{\tau_{at} F^{(k-1)}(0)}{\tau_r F^{(k-1)}(0)} = \frac{\tau_{at}}{\tau_r} \ll 1 \end{aligned}$$

$\rho^{(k)}(t) \simeq \rho^{(k-1)}(t) \cdot \tau_r^{-1}$ and $F^{(k)}(0) = F^{(k-1)}(0) E_A^{-1} = F^{(k-1)}(0) \cdot \tau_a$ follows from the previous assumptions that these functions are

expandable in power series which decline rapidly outside the circles of radius τ_r and E_A respectively.

Our system is thus big enough to neglect higher order terms in the expansion of $\rho(t - \tau)$ (for infinite systems see E. Montrolls¹³⁾ treatment). These achievements shall allow us to rewrite equ. (42) for an asymptotic density matrix, defined over the coarser energy scale $\Delta E'$. Since all functions occurring in the collision terms are smooth enough, \mathcal{F}_0 from equ. (42) may be replaced by

$$\mathcal{F}_0 = \Delta E' 2\pi \delta_+(\omega_{\bar{c}B}).$$

The imaginary part of $\delta_+(\omega_{\bar{c}B})$ will give rise to a renormalization of the energy levels which has little effect on the asymptotic solution. We shall, for the sake of simplicity, leave out the principal value integral replacing $\delta_+(\omega)$ by $\frac{1}{2} \delta(\omega)$. We then end up with

$$\begin{aligned} \frac{d\rho_{AB}}{dt} = & -i\omega_{\bar{A}\bar{B}} \rho_{AB} - i \sum_C \left\{ G_A V_{\bar{A}\bar{C}} \rho_{0CB} e^{-i\omega_{\bar{c}B}t} - G_B \rho_{0AC} V_{\bar{C}\bar{B}} e^{-i\omega_{\bar{A}\bar{C}}t} \right\} \\ & - \pi \sum_{C,E} G_A G_B \left\{ V_{\bar{A}\bar{C}} V_{\bar{C}\bar{E}} \rho_{EB} \delta_{CB} - V_{\bar{A}\bar{C}} V_{\bar{E}\bar{B}} \rho_{CE} \delta_{AE} \right. \\ & \left. - V_{\bar{A}\bar{C}} V_{\bar{E}\bar{B}} \rho_{CE} \delta_{CB} + V_{\bar{C}\bar{E}} V_{\bar{E}\bar{B}} \rho_{AC} \delta_{AE} \right\}, \end{aligned} \quad (50)$$

where the δ' represent ordinary Kronecker symbols. Equ. (50) is a master equation with an inhomogeneous term.

It may be worth noting that for the derivation of a master equation the coarser energy scale $\Delta E'$ is not an essential step. The derivation given here yet has the advantage of simplifying the interpretation of dispersion integrals as δ_+ -functions what is not quite so trivial after the first coarse-graining step.

Equ. (50) can in turn be written in terms of the original basis $\{|\alpha\rangle\}$ and generalized to an operator equation

$$(51) \quad \frac{d\rho}{dt} = -i[\mathcal{H}_0, \rho] - \pi[\bar{V}, [\bar{V}, \rho]_{(d)}] - i[\bar{U}, e^{-i\mathcal{H}_0 t} \rho_0 e^{i\mathcal{H}_0 t}],$$

where $[\bar{V}, \rho]_{(d)}$ denotes the diagonal part of the commutator $[\bar{V}, \rho]$, and \bar{V} is an operator the matrix elements of which are smooth functions over the energy scale, the characteristic energy interval for a change of $\bar{V}_{\alpha\beta}$ being $\Delta E'$. \bar{U} may be defined as

$$(52) \quad \begin{aligned} \bar{V} &= \sum_{\alpha, \beta} |\alpha\rangle \bar{V}_{\alpha\beta} \langle\beta| \\ &= \sum_{A, B} \sum_{\substack{\alpha \in A \\ \beta \in B}} |\alpha\rangle V_{AB} \langle\beta| \end{aligned}$$

Note that $\bar{V}_{\alpha\beta}$ is a real symmetric matrix, just like $V_{\alpha\beta}$ itself, since the basis we are using contains real bound functions only.

4) The Character of the Solutions

Equ. (51), by virtue of its inhomogeneous term, may have solutions which behave oscillatory at infinite times. It is therefore necessary to prove that a relaxing asymptotic solution $\rho(t)$ exists which fulfills the requirements A and B stated in chpt. 3. As main reason for a relaxing $\rho(t)$ to exist we shall find the smoothness of ρ_0 over the energy scale, with other words, the condition that the time τ_m , allowed for preparation of the initial state, has to be such that $\tau_m \ll \tau_r$. If we could prepare initial states in an arbitrary way we might well be able to choose ρ_0 such that the asymptotic $\rho(t)$ remains oscillatory.

The homogeneous part of equ. (51) has to be treated first. To that behalf we have to investigate the underlying eigenvalue problem,

$$(53) \quad \mathcal{L} \rho^{(q)} = -i [\mathcal{H}_0, \rho^{(q)}] - \pi [\bar{V}, [\bar{V}, \rho^{(q)}]_{(\alpha)}] = \lambda_q \rho^{(q)}$$

This operator equation may now be turned into a matrix equation by introducing a basis $\{|\alpha\rangle\}$. Considering the smoothness of $\bar{V}_{\alpha\beta}$ over energy intervals $\Delta E'$ one should keep in mind that the eigenvalue-problem (53) over the basis $\{|\alpha\rangle\}$ can readily be contracted in the same way as equ (39) was summed and smoothed over all $\alpha \in a$ and $\beta \in b$, respectively all $a \in A$ and $b \in B$. The basis $\{|\alpha\rangle\}$ is used here for simplicity of writing only. $\{|\alpha\rangle\}$ may be truncated to a finite set by eliminating all $|\alpha\rangle$ with $E_\alpha > E_{\max}$, where E_{\max} is an energy above which the occupation density of the levels is negligibly small.

Equ. (53) can then be solved within the linear vector space of n-th order square matrices over the field of complex numbers.

In that case we have to define the inner product as

$$(p^{(1)}, p^{(2)}) = \sum_{\alpha, \beta} p_{\alpha\beta}^{(1)*} p_{\alpha\beta}^{(2)}$$

and assume the $p^{(q)}$ to be normalised so that

$$(p^{(q)}, p^{(q)}) = 1$$

Now we can show the following:

- T1) Symmetric eigenmatrices of equ. (53) belong to zero eigenvalues and are diagonal.

Let $p^{(\tilde{q})}$ be any symmetric eigenmatrix, then the collision term will be zero, since \bar{V} is symmetric and therefore $[\bar{V}, p^{(\tilde{q})}] = 0$. From the quadratic form of \mathcal{L} remains only

$$-i(p^{(\tilde{q})}, [\mathcal{H}_0, p^{(\tilde{q})}]) = \lambda_{\tilde{q}}$$

or

$$\lambda_{\tilde{q}} = -i \sum_{\alpha, \beta} p_{\alpha\beta}^{(\tilde{q})*} [\mathcal{H}_0, p^{(\tilde{q})}]_{\alpha\beta} = -i \sum_{\alpha, \beta} \omega_{\alpha\beta} |p_{\alpha\beta}^{(\tilde{q})}|^2 = 0,$$

since the sum changes sign when interchanging α and β .

Furthermore, from

$$-i[\mathcal{H}_0, p^{(\tilde{q})}] = 0$$

or

$$-i \omega_{\alpha\beta} p_{\alpha\beta}^{(\tilde{q})} = 0$$

follows

$$p_{\alpha\beta}^{(\tilde{q})} = 0 \quad \text{for } \alpha \neq \beta$$

- T2) If all $\bar{V}_{\alpha\beta} \neq 0$ the nonvanishing eigenvalues have a negative real part.

$p^{(\tilde{q})}$ shall denote a non-symmetric eigenmatrix. Then

$$\begin{aligned}
 (\hat{\rho}^{(\hat{q})}, \mathcal{L} \hat{\rho}^{(\hat{q})}) &= -i(\hat{\rho}^{(\hat{q})}, [\mathcal{H}_0, \hat{\rho}^{(\hat{q})}]) - \pi(\hat{\rho}^{(\hat{q})}, [\bar{\nu}, [\bar{\nu}, \hat{\rho}^{(\hat{q})}]_{(\alpha)}]) \\
 &= -i \sum_{\alpha\beta} \hat{\rho}_{\alpha\beta}^{(\hat{q})*} [\mathcal{H}_0, \hat{\rho}^{(\hat{q})}]_{\alpha\beta} - \pi \sum_{\alpha\beta} \hat{\rho}_{\alpha\beta}^{(\hat{q})*} \bar{V}_{\alpha\beta} \{ [\bar{\nu}, \hat{\rho}^{(\hat{q})}]_{\beta\beta} - [\bar{\nu}, \hat{\rho}^{(\hat{q})}]_{\alpha\alpha} \} \\
 &= -i \sum_{\alpha\beta} \omega_{\alpha\beta} \hat{\rho}_{\alpha\beta}^{(\hat{q})*} \hat{\rho}_{\alpha\beta}^{(\hat{q})} - \pi \sum_{\alpha} [\hat{\rho}^{(\hat{q})+}, \bar{\nu}]_{\alpha\alpha} [\bar{\nu}, \hat{\rho}^{(\hat{q})}]_{\alpha\alpha} \\
 &= -i \sum_{\alpha\beta} \omega_{\alpha\beta} |\hat{\rho}_{\alpha\beta}^{(\hat{q})}|^2 - \pi \sum_{\alpha} |[\bar{\nu}, \hat{\rho}^{(\hat{q})}]_{\alpha\alpha}|^2 = \lambda_{\hat{q}},
 \end{aligned}$$

thus $\text{Re } \lambda_{\hat{q}} < 0$.

The condition $\bar{V}_{\alpha\beta} \neq 0$ for all α and β seems rather strong, even if it is very unlikely that one of these matrix elements will vanish. However, for establishing a physically relevant solution of (51) we only need the requirement that $\bar{V}_{ab} \neq 0$, what will be fulfilled in all conceivable cases.

By means of T1 and T2 it is also easy to see that the eigenvalues $\lambda_{\hat{q}}$, belonging to non-diagonal eigenmatrices, are non-degenerate and that any two such $\hat{\rho}^{(\hat{q})}$ are linearly independent.

The homogeneous equation (51) will then have the solution

$$(54) \quad \hat{\rho}_h(t) = \sum_q \hat{\rho}^{(q)} d_q e^{\lambda_q t}$$

where the d_q , are uniquely determined by $\hat{\rho}_0$, namely

$$\hat{\rho}_0 = \sum_q \hat{\rho}^{(q)} d_q.$$

We shall first look at the diagonal part of $\rho(t)$. In this case only the inhomogeneous term may play any role:

$$\begin{aligned} \frac{d\rho_{\alpha\alpha}}{dt} &= -i [\bar{V}, e^{-i\mathcal{H}_0 t} \rho_0 e^{i\mathcal{H}_0 t}] \\ &= \sum_{\gamma} \bar{V}_{\alpha\gamma} (\rho_{0\gamma\alpha} e^{-i\omega_{\gamma\alpha} t} - \rho_{0\alpha\gamma} e^{-i\omega_{\alpha\gamma} t}) \end{aligned}$$

The γ -sum can be converted into an integral readily. ρ_0 is a real, symmetric matrix, therefore

$$\begin{aligned} (55) \quad \rho_{\alpha\alpha}(t) - \rho_{0\alpha\alpha} &= 2\pi \sum_{\gamma} \bar{V}_{\alpha\gamma} (\rho_{0\gamma\alpha} \delta_+(\omega_{\gamma\alpha}) - \rho_{0\alpha\gamma} \delta_+(\omega_{\alpha\gamma})) \\ &= 0. \end{aligned}$$

As one might have expected beforehand the occupation of the eigenstates of \mathcal{H}_0 in the ensemble does not change in time since there are no external collisions and we are dealing with the time-asymptote of the density matrix.

For obtaining the solution of the inhomogeneous equation we have to expand the inhomogeneous part in terms of the eigenmatrices $\rho^{(q)}$. As the diagonal part of the inhomogeneous term is zero we shall have non-symmetric eigenmatrices in the expansion only. Denoting the indices of non-symmetric matrices by \hat{q} , we have

$$(56) \quad -i[\bar{V}, e^{-i\mathcal{H}_0 t} \rho_0 e^{i\mathcal{H}_0 t}] = \sum_{\hat{q}} \rho^{(\hat{q})} f_{\hat{q}}(t)$$

The general form of $f_{\hat{q}}(t)$ needs to be worked out for later conclusions. Using the linear independence of the $\rho^{(q)}$ we can form the inner product of equ.(56) with $\rho^{(\hat{r})}$:

$$\begin{aligned} \sum_{\hat{q}} (\rho^{(\hat{r})}, \rho^{(\hat{q})}) f_{\hat{q}}(t) &= -i \sum_{\alpha\beta\gamma} \rho_{\alpha\beta}^{(\hat{r})*} (\bar{V}_{\alpha\gamma} \rho_{\gamma\beta} e^{-i\omega_{\gamma\beta}t} - \rho_{\alpha\gamma} \bar{V}_{\gamma\beta} e^{-i\omega_{\alpha\gamma}t}) \\ &= -i \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} \rho_{\gamma\beta} \sum_{\alpha} \rho_{\alpha\beta}^{(\hat{r})*} (\bar{V}_{\alpha\gamma} - \bar{V}_{\beta\alpha}) \\ (57) \quad &= -i \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} R_{\beta\gamma}^{(\hat{r})}, \end{aligned}$$

$$(57a) \quad R_{\beta\gamma}^{(\hat{r})} = \rho_{\alpha\beta} \sum_{\alpha} \rho_{\alpha\beta}^{(\hat{r})*} (\bar{V}_{\alpha\gamma} - \bar{V}_{\beta\alpha}).$$

Denoting

$$D = \det(\rho^{(\hat{r})}, \rho^{(\hat{q})})$$

and the adjoint determinant of D by $D^{\hat{r},\hat{q}}$, we can obtain $f_{\hat{q}}(t)$ from equ.(57) by

$$\begin{aligned} f_{\hat{q}}(t) &= -\frac{i}{D} \sum_{\hat{r}} D^{\hat{r},\hat{q}} \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} R_{\beta\gamma}^{(\hat{r})} \\ (58) \quad &= \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} \left(\frac{-i}{D} \sum_{\hat{r}} D^{\hat{r},\hat{q}} R_{\beta\gamma}^{(\hat{r})} \right) \\ &= \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} \cdot Q_{\beta\gamma}^{(\hat{q})} \end{aligned}$$

We can easily see now that $Q_{\beta\gamma}^{(\hat{q})}$ is a smooth function of E_{β} and E_{γ} . This will be so if $R_{\beta\gamma}^{(\hat{r})}$ is a smooth function of these variables. By (57a) we can see that $R_{\beta\gamma}^{(\hat{r})}$ depends in a smooth way \wedge only if $\rho_{\alpha\beta}^{(\hat{r})}$ depends smoothly on E_{β} . This can be seen by looking at equ.(52) for the eigenvector $\rho^{(\hat{q})+}$, belonging to an eigenvalue $\lambda_{\hat{q}}^*$ and forming the $\beta\alpha$ -matrix elements:

$$-i\omega_{\beta\alpha} \rho_{\alpha\beta}^{(\hat{r})*} - \sum_{\gamma} \bar{V}_{\beta\alpha} \bar{V}_{\alpha\gamma} (\rho_{\alpha\gamma}^{(\hat{r})*} - \rho_{\gamma\alpha}^{(\hat{r})*}) = \lambda_{\hat{q}}^* \rho_{\alpha\beta}^{(\hat{r})*}$$

or

$$p_{\alpha\beta}^{(\hat{r})} = \frac{\pi}{i\omega_{\alpha\beta} + \lambda_{\hat{q}}} \sum_{\gamma} \bar{V}_{\beta\alpha} \bar{V}_{\alpha\gamma} (p_{\alpha\gamma}^{(\hat{r})} - p_{\gamma\alpha}^{(\hat{r})})$$

Therefore $p_{\alpha\beta}^{(\hat{r})}$ depends on E_{β} as smooth as $\bar{V}_{\beta\alpha}/(i\omega_{\alpha\beta} + \lambda_{\hat{q}})$, what is perfectly sufficient to convert the γ -sum in (58) into an integral.

The total solution of equ. (51) then has the form

$$\begin{aligned} p(t) &= \sum_{\hat{q}} p^{(\hat{q})} d_{\hat{q}} e^{\lambda_{\hat{q}} t} + \sum_{\hat{q}} p^{(\hat{q})} e^{\lambda_{\hat{q}} t} \int_0^t e^{-\lambda_{\hat{q}} \tau} f_{\hat{q}}(\tau) d\tau \\ (58) \quad &= p_{0(d)} + \sum_{\hat{q}} p^{(\hat{q})} d_{\hat{q}} e^{\lambda_{\hat{q}} t} + \sum_{\hat{q}} p^{(\hat{q})} e^{\lambda_{\hat{q}} t} \int_0^t e^{-\lambda_{\hat{q}} \tau} f_{\hat{q}}(\tau) d\tau \end{aligned}$$

where $p_{0(d)}$ is the diagonal matrix representing the diagonal part of p_0 . According to T1 all $\lambda_{\hat{q}}$ have a non-vanishing ^{negative} real part, therefore the terms under the first sum are damped exponentially, but this is not immediately clear for the terms under the second sum of equ. (58). We have

$$\begin{aligned} e^{\lambda_{\hat{q}} t} \int_0^t e^{-\lambda_{\hat{q}} \tau} f_{\hat{q}}(\tau) d\tau &= \sum_{\beta\gamma} e^{\lambda_{\hat{q}} t} Q_{\beta\gamma}^{(\hat{q})} \int_0^t e^{(-i\omega_{\beta\gamma} - \lambda_{\hat{q}}) \tau} d\tau \\ (59) \quad &= \sum_{\beta\gamma} \frac{e^{-i\omega_{\beta\gamma} t} - e^{\lambda_{\hat{q}} t}}{-i\omega_{\beta\gamma} - \lambda_{\hat{q}}} Q_{\beta\gamma}^{(\hat{q})} \end{aligned}$$

The second term under the sum is again damped, so we focus attention on the first:

$$\sum_{\beta\gamma} \frac{e^{-i\omega_{\beta\gamma}t}}{-i\omega_{\beta\gamma}-\lambda_q} Q_{\beta\gamma}^{(\hat{q})} = \int_0^\infty dE_\gamma dE_\beta \sigma(E_\beta) \sigma(E_\gamma) \frac{e^{-i\omega_{\beta\gamma}t}}{-i\omega_{\beta\gamma}-\lambda_q} \cdot Q^{(\hat{q})}(E_\beta, E_\gamma)$$

where $\sigma(E)$ is the density of states. By the substitution

$$\begin{aligned} E_\beta &= E \\ E_\gamma &= \frac{z}{t} + i\lambda_q + E \end{aligned}$$

this goes over into

$$e^{\lambda_q t} \int_0^\infty dE \sigma(E) \int_{-(E+i\lambda_q)t}^{\infty-i\lambda_q t} \sigma\left(\frac{z}{t} + E + i\lambda_q\right) Q^{(\hat{q})}\left(E, \frac{z}{t} + E + i\lambda_q\right) \frac{e^{-iz}}{-iz} dz$$

The integration path of the inner integral is from the point $-(E+i\lambda_q)t$, which is lying in the positive half-plane, parallel to the real axis to $+\infty$. The distance of the integration path from the real axis is of the order of magnitude 1, since

$$t \simeq \tau_q \simeq \overline{\operatorname{Re} \lambda_q}^{-1}$$

We then extend the integrand analytically and close the integral path C by encircling the negative imaginary half-plane clockwise, coming back to the point $-(E+i\lambda_q)t$ which is of the order infinity under the outer integral. We obtain

$$\begin{aligned} & e^{\lambda_q t} \int_0^\infty dE \sigma(E) \int_C \sigma\left(\frac{z}{t} + E + i\lambda_q\right) Q^{(\hat{q})}\left(E, \frac{z}{t} + E + i\lambda_q\right) \frac{e^{-iz}}{-iz} dz \\ &= i e^{\lambda_q t} \int_0^\infty dE \sigma(E) \sigma(E + i\lambda_q) Q^{(\hat{q})}(E, E + i\lambda_q) \end{aligned}$$

This shows that the terms in the second sum of (58) are indeed damped exponentially.

5) Conclusion

We were able to derive a master equation for an ensemble of isolated molecules. It should be borne in mind, however, that the statement of equilibrium for the molecular system by some kind of experiment is bound to a time scale τ_{eq} of the order

$$\tau_{eq} \ll \tau_{tr}$$

The necessary requirements were of a rather general nature and likely to be fulfilled for molecules with 6 or more atoms. Inequality (40) will always hold if \bar{V} is sufficiently small, as can easily be seen by eqs. (54) and (41a). Furthermore, the smoothness of V_{ab} , guaranteed by conditions A1)-A3), can hardly be thought to be not fulfilled in any non-pathological case. It was mentioned before that the requirements B1)-B4) are not essential in deriving the master equation. They may, however, in practice play an important role for condensing the original set of equations to a lower order. In many instances condensation may be possible to an extent where the range of energy involved is divided into 10 intervals only and yet allows to describe the relaxation process with sufficient accuracy. Estimation of such very coarse matrix-elements V_{AB} , partly by experiment, is then not inconceivable any more.

A crude way of determining by order of magnitude the rate of an intramolecular rearrangement reaction (in the region where it is of first order) would be to use a suitable average over the $Re \lambda_q$ as a rate coefficient. Determining τ_r such that

$$\sum_q e^{Re \lambda_q \cdot \tau_r} = 1$$

we could use

$$\bar{k} \approx \frac{1}{\tau_r}$$

as a rate coefficient.

According to the outline in chpt.2 the complete expression for the rate will be

$$R = \frac{d}{dt} \text{tr}(K \bar{\rho}) = \text{tr}\left(K \frac{d\rho}{dt}\right)$$

The general form of $\rho(t)$ is

$$\rho(t) = \rho_0(\alpha) + \sum_{\hat{q}} \rho^{(\hat{q})} e^{\lambda_{\hat{q}} t} F_{\hat{q}}$$

and

$$\frac{d\rho}{dt} = \sum_{\hat{q}} \rho^{(\hat{q})} \lambda_{\hat{q}} e^{\lambda_{\hat{q}} t} F_{\hat{q}}$$

so that

$$(60) \quad R = \sum_{\hat{q}} \lambda_{\hat{q}} e^{\lambda_{\hat{q}} t} F_{\hat{q}} \text{tr}(K \bar{\rho}^{(\hat{q})})$$

R by equ. (60) is a real quantity because the eigenvalues appear pairwise, i.e. if $\lambda_{\hat{q}}$ is an eigenvalue $\lambda_{\hat{q}}^*$ is also one.

Finally we may study the mechanism in an intramolecular conversion reaction including vibrational relaxation after external collisions. Though we did not include external collisions explicitly in the description of the relaxation process we can make use of the master equation (51) for the period between collisions. If the duration of an external collision is short compared with the time between collisions, τ_{coll} , we may again specify an initial density ρ_0^I by a set

of commuting observables. ρ_o^I is then the initial state of an ensemble representing wave packets which are localized onto configuration I. Applying equ. (51) we can say the following: ρ_o^I will, in an eigenrepresentation of \mathcal{H}_o , have large elements far from the diagonal. In the expansion of ρ_o^I in terms of the eigenmatrices $\rho^{(q)}$,

$$\rho_o^I = \sum_q \rho^{(q)} \alpha_q^I,$$

there will large α_q^I occur for highly unsymmetric $\rho^{(q)}$. By equation (54), the negative real parts of the eigenvalues corresponding to these eigenmatrices are the largest. Thus, the parts of the density matrix far from the diagonal will quickly be damped away. We arrive at the same result if we set up equ. (51) for a density matrix $\rho^I(t)$ with \mathcal{H}_o^I instead of \mathcal{H}_o . From the latter case we can see immediately that

$$\lim_{t \rightarrow \infty} \rho^I(t) = \rho_o,$$

ρ_o being the one defined in chpt.2 and the relaxation time τ_r^I for this process may be used to determine the order of the observation time τ_m , for identifying the initial state of the species I,

$$\tau_m \simeq \tau_r^I$$

Thus, if $\tau_r^I \ll \tau_{coll}$ and τ_r , what will usually be the case, and also the characteristic change of the diagonal elements of ρ by the external collisions is slow compared with τ_r , equ.(51) will give the correct rate for the isomerization reaction.

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